Chapter

Synthesis and Catalytic Activity Studies of Silver Nanoparticles Stabilized in Polymeric Hydro Gel

Jaya T. Varkey

Abstract

Silver nanoparticles (AgNPs) are one of the most vital and fascinating nanomaterials among several metallic nanoparticles that are involved in biomedical applications. But their stabilization towards agglomeration is a serious concern. Synthesized silver nanoparticles can be dispersed in polymeric hydrogel for stabilization and can be efficiently used in heterogeneous catalysis. Polystyrene crosslinked with 1, 6-hexanediol diacrylate can be suitably functionalized for catalytic activities. The nature of the support has a profound influence on the reactivity of the polymeric resin. A flexible support with optimum hydrophilic and hydrophobic balance enhanced the reactivity of the supporting system. Using this supported AgNPs catalytic reduction of Para-nitro phenol can be easily accomplished comparing to conventional method.

Keywords: Silver nano, polymer, hydrogel, catalyst, P-Nitrophenol

1. Introduction

Nanomaterials may offer novel answers for technological challenges in various areas, like medicine, solar energy conversion, catalysis, and water treatment. Nanoparticles exhibit improved activities compared to their parent metal atoms because of their increased surface area [1]. These usual activities may find applications in different fields such as catalysis, biosensing, imaging and drug delivery [2–8]. But significant problem with the synthesis of nanoparticles is their stabilization. Crosslinked polymers with suitable functionality can be used as an efficient support for incorporating nano particles. Polymer embedding represents the simplest way to protect the nanoparticles and providing a means of stabilization in handling and applications [9]. The incorporation of Ag NPs in the polymeric hydrogel matrix facilitates the recycling of catalyst without reducing the catalytic efficiency. In polymer supported catalysis, Styrene-divinyl benzene (PS-DVB) copolymer is the most used supporting system. Due to the hydrophobic and rigid nature of polymer backbone, PS-DVB systems show low metal ion uptake. Comparing to that 1, 6-hexanediol diacrylate (HDODA) cross-linked polystyrene (PS HDODA) possess optimum hydrophobic hydrophilic balance and is more flexible than PS–DVB system [10]. Thus PS-HDODA has been introduced as a more convenient catalyst support than PS-DVB system.

1.1 Silver nanoparticles

Silver nanoparticles are nanoparticles of silver of between 1 nm and 100 nm in size. AgNPs are one of the most crucial and interesting nanomaterials among various metallic nanoparticles that are involved in biomedical applications. AgNPs play a major role in nano chemistry, particularly in nanomedicine due to their antibacterial properties. Although several noble metals have been used for many applications, AgNPs have been concentrated on potential applications in cancer diagnosis and therapy [11]. Due to their distinct properties, they have been used for several applications, including as antibacterial agents, in industrial, household, and healthcare-related products, consumer products, medical device coatings, optical sensors, and cosmetics. Also found applications in pharmaceutical industry, diagnostics, drug delivery, as anticancer agents, and have enhanced the tumor-killing effects [12]. To accomplish the requirement of AgNPs for these applications, several methods have been adopted for its synthesis. But the conventional physical and chemical methods seem to be very expensive and hazardous. An efficient method for synthesizing and stabilizing silver nanoparticles is reported.

The challenges in the application of nano particles could be overcome by incorporation into hydro gels [13]. A hydrogel is a network of crosslinked polymer chains that are hydrophilic in nature. Such polymer supported catalyst systems can be separated from the products by means of simple filtration which led to operational flexibility [14]. Immobilized metal nano particles find application in several fields such as water treatment, food processing, catalysis etc. [15]. Silver nano particles stabilized in sulphonated 1,6-Hexanediol diacrylate (HDODA) cross-linked polystyrene were obtained by in situ reduction of silver nitrate in the hydrogel network. Hydro gel network is a carrier where the in situ reduction of $AgNO_3$ in the presence of $NaBH_4$ as reducing agent occurred.

1.2 Polymeric hydrogel

Hydrogels are cross-linked polymeric networks, which have the potential to carry water within the spaces available among the polymeric chains. The hydrogels have been used extensively in various biomedical applications like drug delivery, cell carriers and entrapment, wound management, and tissue engineering. The ability of hydrogels to hold water arises from the presence of hydrophilic functional groups attached to the polymeric backbone. Due to their crosslinking nature among polymer chains, they are insoluble in solvent systems. Many materials including both naturally occurring and synthetic, fit the definition of hydrogels. A polymeric material can act as a hydrogel when it exhibits the ability to swell and retain a significant fraction of water within its structure but will not dissolve in water. Hydrogels have received considerable attention in the past 50 years, due to their exceptional promise in wide range of applications [16]. They possess a degree of flexibility very similar to natural tissue due to their large water content. The ability of hydrogels to absorb water occurs from the hydrophilic functional groups attached to the polymeric backbone, while their resistance to dissolution attributes to cross-links between network chains. Polystyrene-DVB systems cannot act as efficient hydrogel systems due to their rigid and hydrophobic nature. But if DVB is changed to a flexible crosslinker like Hexanediol diacrylate (HDODA) the system could act as a hydrogel. This is due to the hydrophobic-hydrophilic balance and the flexible nature of the crosslinker (**Figures 1** and **2**).

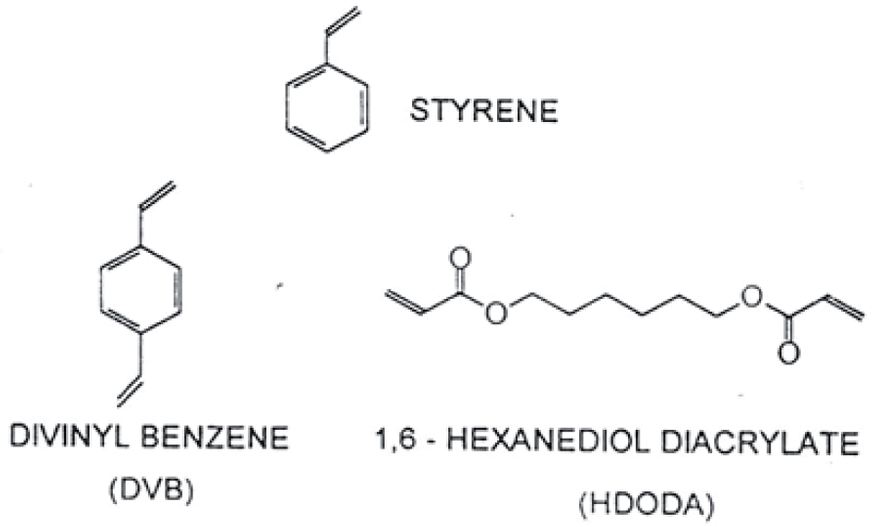

Figure 1.
Structural comparison of DVB and HDODA.

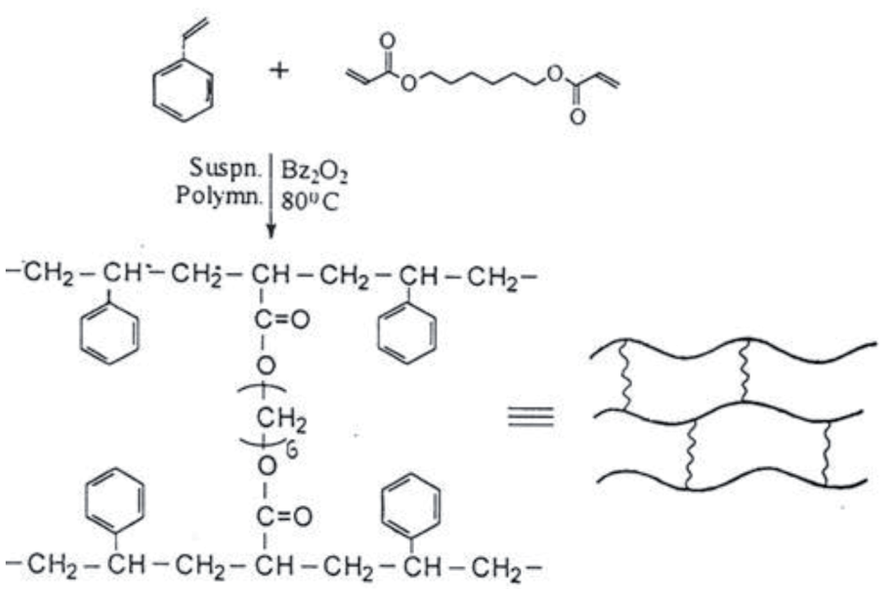

Figure 2.
Scheme of polymer preparation by suspension method.

1.3 Functionalization

Functionalized polymer networks [17] have gained great importance in many fields of scientific research as well as for industrial applications, which will still increase because of the variety of possible modifications of their chemical and physical properties. Macro porous polymer networks prepared from styrene (S) and divinylbenzene (DVB) can act as ion exchange resins after functionalization with sulfonic acid groups. This can play an important role as solid acid catalysts in heterogeneous catalysis. The large amount of work that has been done until now to investigate the catalytic properties of sulfonated PS-DVB polymer have clearly shown that both their catalytic activity and selectivity are dependent on different parameters which are interconnected in a complicated manner. Besides structure and crosslinking density of the polymeric network influences the swelling capacity of the polymeric systems. The catalytic activity depends on the distribution and the

local concentration of the sulfonic acid groups in the polymeric network. Various methods for the synthesis of tailor-made functional networks are important for the development of new and improved catalysts. But the rate of sulphonation depends on the flexibility and hydrophilicity of the polymer support. The DVB-crosslinked polystyrene particles are so dense and hydrophobic that it is difficult for the hydrophilic sulfonation agent to enter the internal volume of the particles without the swelling agent. PS-HDODA support has more flexibility and optimum hydrophilic - hydrophobic balance than the conventional PS-DVB resin.

1.4 Sulfonation

Surface functionalization of porous polymer networks was investigated using the sulfonation. Functionalization of the polymer support can be done by using sulfuric acid. The rate of sulfonation depends on the composition of the sulfuric acid used. An increase in the concentration of sulfuric acid (**Figure 3**) leads to higher functionalization capacities within the same reaction time. PS-HDODA resin is functionalized by sulfonation and introduced both as an ion exchanger and as a catalyst support for heterogeneous catalysis. The degree of sulfonation can be controlled by varying the reaction time.

1.5 Ion-exchange capacity measurements

Ion-exchange capacity is the measure of the ability of an insoluble material like crosslinked polymeric supports to undergo shifting of ions attached to it which are loosely incorporated into its structure with oppositely charged ions present in the surrounding solution. Salt splitting titration is used for the determination of ion-exchange capacity of the sulfonated resin. Here the salts of carboxylic acids are decomposed to its acid and base compounds. In this process the salt is passed through ion exchange resins and the corresponding electrochemical reaction occurs and splitting takes place. The ion exchange membranes help to separate the metallic

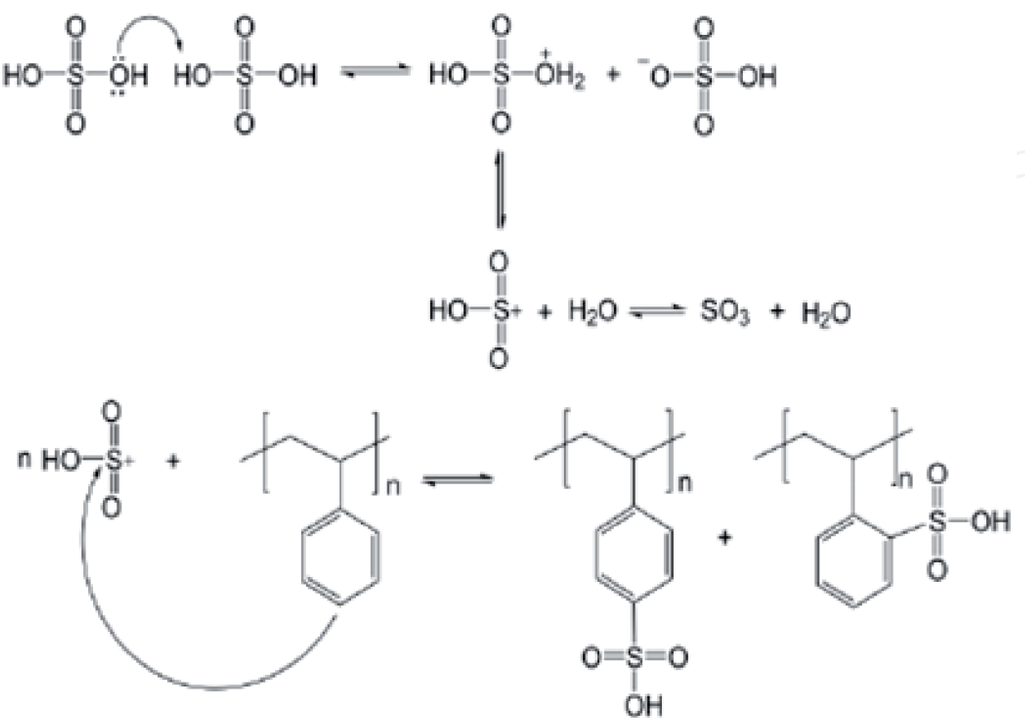

Figure 3.
Mechanism of Sulphonation reaction [18].

and acidic ions. The ion-exchange capacity of the sulphonated resin (IEC, meq/g) was calculated from the following equation.

$$IEC = c \times v / w \quad (1)$$

Where 'c' is the standardized concentration of sodium hydroxide, 'v' is the volume (ml) of the NaOH solution at an end point and 'w' is the weight (g) of determined sulphonated resin.

2. Metal loading to the polymeric support

Metal and metal oxide nanoparticles exhibit unique properties about sorption behaviors, magnetic activity, chemical reduction, ligand sequestration, among others. So, they can be effectively used in catalysis and biomedical applications. However, metal and metal oxide nanoparticles lack chemical stability and mechanical strength. Another serious problem is the agglomeration of nanoparticles which can reduce the surface area of the particles. This will lead to decrease in the surface to volume ratio of the particles and eventually bringing down the reaction rate. Proper distribution of nanoparticles into different polymer surfaces can reduce many of these shortcomings without affecting the parent properties of the nanoparticles. Moreover, the polymer support is not acting as an inert support. Proper selection of functional groups on the support may even lead to the enhancement of the properties of nanoparticles. These polymeric hydrogels can be used as microreactors to fabricate nanoparticles. Assembly of Silver nanoparticles into polymeric hydrogel system can be done by chemical reduction of silver ions inside the polymer network.

2.1 Attachment of silver nanoparticles to sulphonated PS-HDODA resin

Silver nanoparticles has found applications in many fields of nanoscience including medicine and catalysis. Also, silver is commonly used in consumer products due to its antibacterial properties. These properties of silver nanoparticles made them in immense number of studies. The various troubles developed while utilizing these nano particles could be controlled by incorporating these into hydro gels. Hydrogels are polymer supports with optimum hydrophobic-hydrophilic balance. Polymer supported catalyst systems can be easily recovered from the products after the reaction by filtration, which leads to operational flexibility. Polymer anchored metal nano particles find applications in various fields such as water treatment, food processing, medicine, and catalysis. A new polymer support, polystyrene crosslinked with HDODA was introduced, which after sulphonation can be effectively used as an efficient support. Silver nano particles incorporated into sulphonated HDODA cross-linked polystyrene were obtained by in situ reduction of silver nitrate in the hydrogel network. Sulphonated PS-HDODA is acting as a hydro gel network and as a carrier where the in situ reduction of $AgNO_3$ in the presence of $NaBH_4$ as reducing agent occurred.

2.2 Catalytic activity of silver nanoparticles stabilized in sulphonated PS-HDODA support

Nanomaterial-based catalysts are usually heterogeneous catalysts broken up into metal nanoparticles to enhance the catalytic process. Metal nanoparticles have high

surface area, which can increase catalytic activity. Nanoparticle catalysts can be easily separated and recycled. The activity of catalytic system does not only depend upon size and shape of nanoparticles immobilized on different stabilizing systems, but it is also affected by stabilizing system. The nature of the support system has a profound influence on the reactivity of the nanoparticles anchored on it.

Para-nitro phenol (p-NP) is a harmful pollutant which is poisonous to living organisms [19]. These are commonly used in the manufacture of pesticides, insecticides, fungicides, and find applications in pharmaceuticals and synthetic dye industry [20]. Living things can get exposed to p-NP by many ways such as inhalation, ingestion, and dermal contact. Adverse effects of p-NP on health depends on duration, exposure dose, pathways, and individual characteristics such as gender, nutritional status, lifestyle etc. Exposure of p-NP by inhalation or ingestion can cause headache, drowsiness, nausea, cyanosis, and eye irritation [21]. One of the most toxic derivatives of the commonly used parathion insecticide is p-NP and it is carcinogenic and cytotoxic [22]. It is highly soluble in water bodies such as fresh water, marine environments and in industrial wastewater and that makes the water sources unhealthy. Because of this high solubility rate removal of p-NP from wastewater is not effective by traditional water purification methods. For water purification from contaminants catalytic approach plays an important role. Catalytic reduction of p-NP to p-Aminophenol which is an important chemical intermediate in the preparation of pharmaceuticals, dyes, pesticides, photographic developers is an efficient solution for the effective removal of p-NP [23–28]. Silver nanoparticles are widely used due to its size, shape, and antibacterial properties. It can be effectively used for the catalytic reduction of p-NP after stabilizing in polymeric PS-HDODA hydro gel. Reduction of p-NP using silver nanoparticles stabilized in sulphonated PS-HDODA resin is an efficient method for its successful removal. $NaBH_4$ can be as used as reducing agent. After catalysis, catalyst can be separated by simple filtration. The percentage catalytic efficiency can be easily calculated.

3. Morphology and Characterization

The surface morphology of the nanoparticles affects the uniform dispersion of NPs in the polymeric hydrogels. These surface properties are significant and that can affect the properties of the hybrid nanocomposite hydrogels. In this regard, the surface fracture of the hybrid hydrogels and the dispersion of Ag NPs in the nanocomposite were analyzed by SEM and TEM.

The surface morphology of the polymer beads was studied by Scanning electron microscopy. Bead forms of the copolymer retain morphology. It was found that the prepared PS-HDODA copolymer beads were having very smooth surface (**Figure 4**). But after sulphonation the external surface of the sulphonated copolymer beads showed scales and cracks indicating effective sulphonation. After the loading of silver nanoparticles, the external surface of the polymer beads became more and more rough, and the morphology has changed as evident from **Figure 4**.

The EDX image (**Figure 5**) of Silver nanoparticles loaded sulphonated PS-HDODA has clearly indicated the presence of metal loaded into the polymer.

The TEM image of sulphonated PS-HDODA resin showed very smooth surface (**Figure 6**). In metal loaded resin, the silver nano particles appeared as dark spot inside sulphonated PS-HDODA resin with the size in the range of approximately 30 nm.

Catalytic approach plays an important role for the purification of water from hazardous contaminants. Sodium borohydride reduction of p-NP using the silver nanoparticles loaded sulphonated PS-HDODA resin is a useful reaction to study

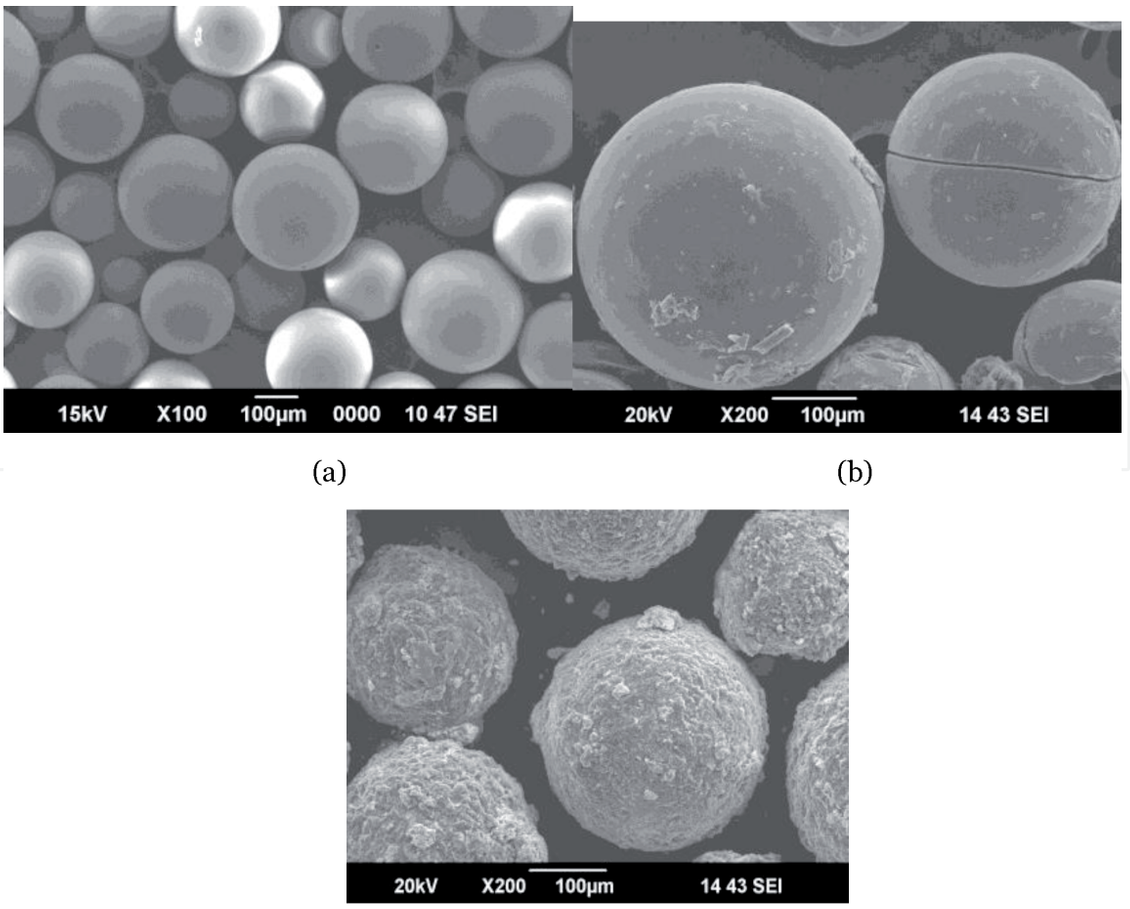

Figure 4.
SEM image of (a) PS-HDOD a resin, (b) Sulphonated PS-HDODA resin, (c) silver nanoparticles loaded sulphonated PS-HDODA resin.

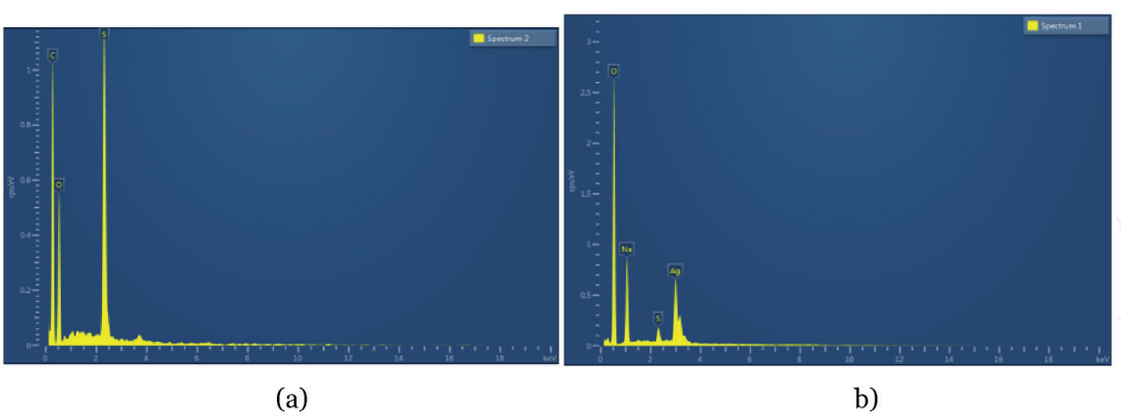

Figure 5.
EDX image of (a) Sulphonated PS-HDODA resin, (b) silver nanoparticles loaded sulphonated PS-HDODA resin.

the catalytic activity of supported silver nanoparticles (**Figure 7**). The percentage catalytic efficiency was calculated using the following equation.

$$\%\text{efficiency} = \text{Co} - \text{C} / \text{Co}\ \text{X}\ 100. \quad (2)$$

Where 'Co' is the initial absorbance of p-NP and 'C' is the absorbance of p-NP at the time t. From the percentage efficiency plot (**Figure 8**), as time increases the

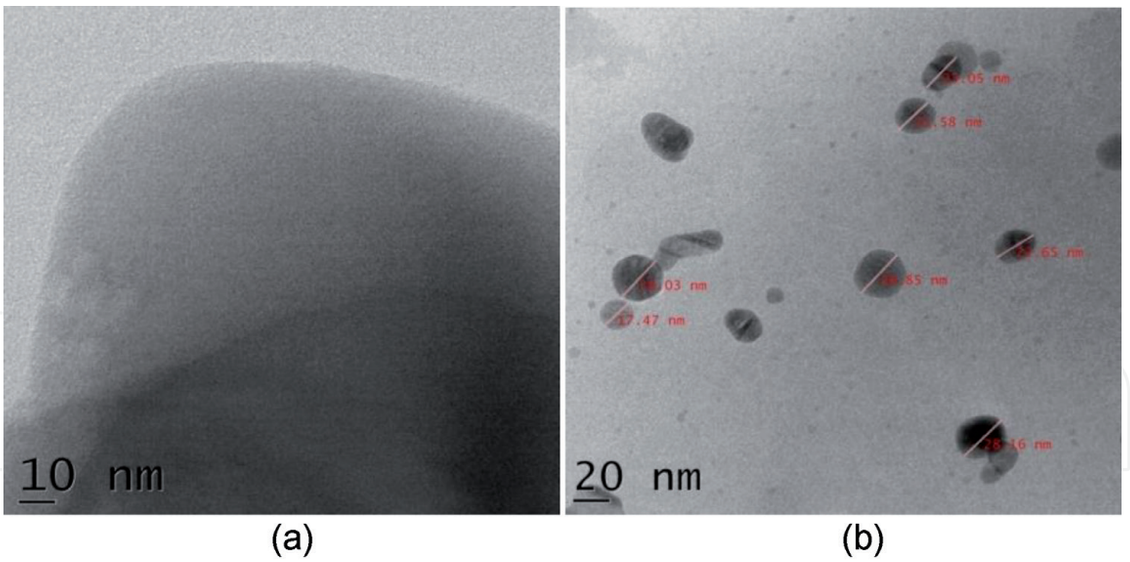

Figure 6.
TEM image of (a) Sulphonated PS-HDODA resin, (b) silver nanoparticles loaded sulphonated PS-HDODA resin.

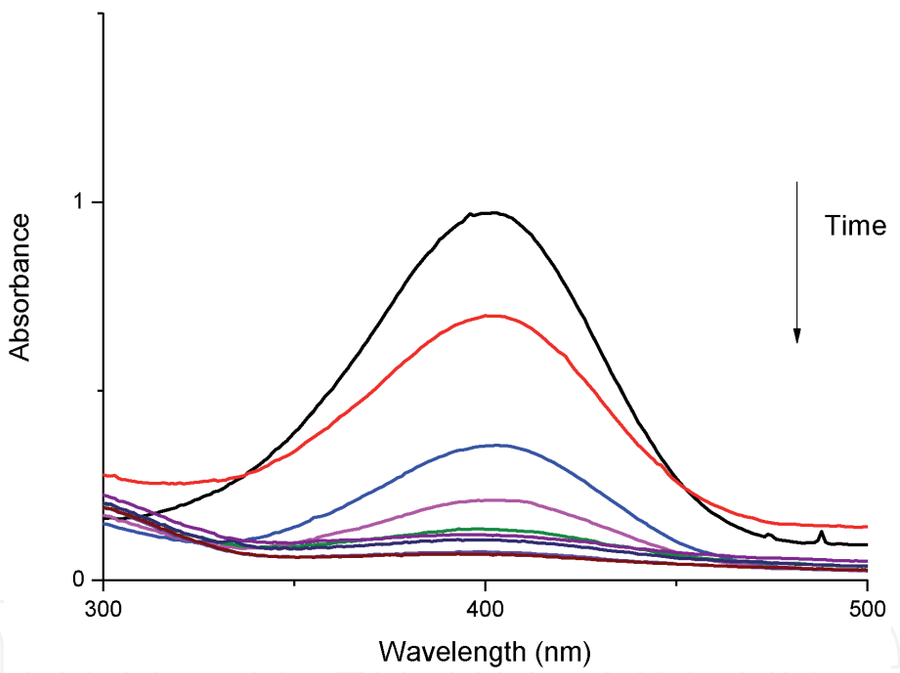

Figure 7.
UV- visible absorbance spectra for catalytic reduction of p-NP.

efficiency of the catalyst was also increased. From the experimental data the rate of the reaction corresponds to first order kinetics.

$$\ln C / Co = -kt. \quad (3)$$

Where Co is the initial absorbance of the reaction system, C is the absorbance at time t. From kinetic curve rate constant k was calculated for the reaction system (**Figure 9**).

In the FTIR spectrum the resins exhibited a band around 1720–1724 cm^{-1} indicating carbonyl stretching frequency, which is an indication HDODA cross-linking to the polymeric support system. Bands at 1598–1657 cm^{-1}, 1473–1493 cm^{-1} and 1443–1451 cm^{-1} corresponds to phenyl ring stretching vibrations of it C=C-C

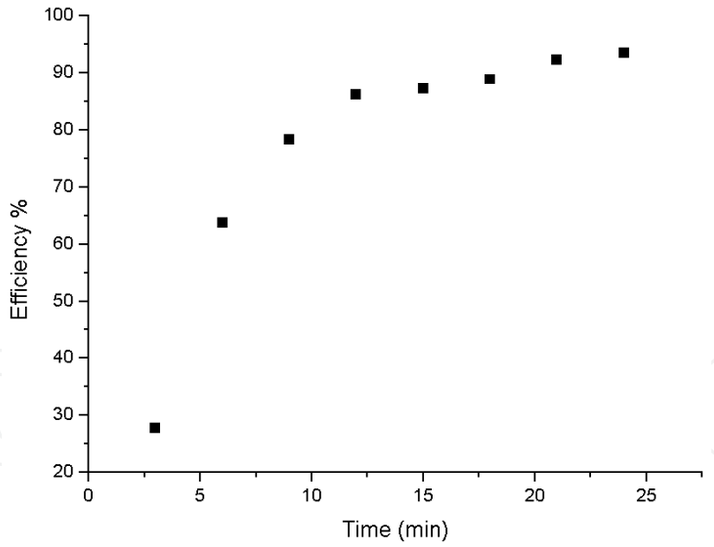

Figure 8.
Efficiency % with irradiation time for catalytic reduction of p-NP.

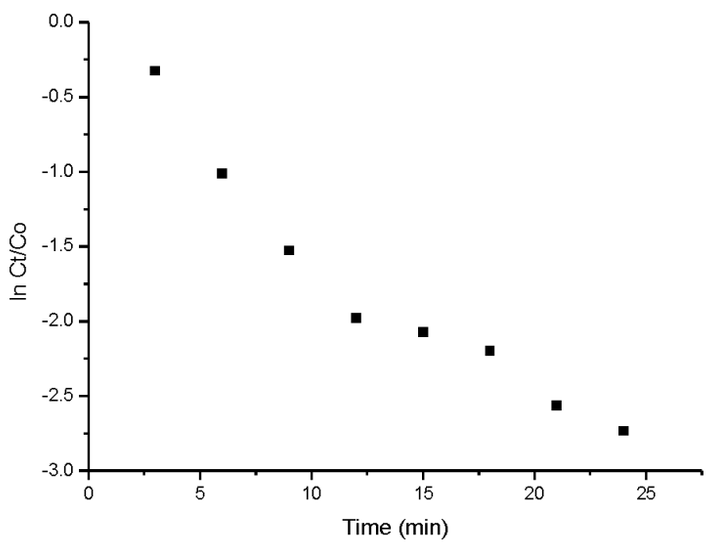

Figure 9.
Kinetic curves for p-NP reduction.

conjugative system. The frequency in the range 1166 cm^{-1} was attributed to S=O symmetric stretching vibration. When silver metal nanoparticles loaded the S=O stretching frequency lowered to 1130 cm ^{1}. 1033–1078 cm^{-1} and 907 cm^{-1} represented phenyl in-plane and out of plane C-H bending vibrations respectively. 700–759 cm^{-1} phenyl ring wagging and twisting, respectively.

4. Conclusion

Polymers found application in many fields because of their highly useful properties such as high strength, low weight, and low cost of preparation. Although polymers are essential to modern society, several major challenges block their uses in many fields. One of the major problems is that almost majority of world's supply of polymeric materials is derived from fossil resources, which is a resource that is consuming rapidly and affects the environment significantly. A potential solution to both challenges is to replace fossil fuel-derived polymers with those produced from renewable resources.

The polymer support obtained by the copolymerization of Styrene and HDODA can be effectively used in polymer supported reactions. Suspension polymerization can be used for the efficient synthesis of copolymer beads. PS-HDODA copolymer beads were converted into hydro gel by sulphonation of the cross-linked polymer. Metal loaded to this polymeric support was converted into nano scale by sodium borohydride reduction. Preparation of silver nano particles stabilized in this polymeric hydro gel can be used as an efficient catalyst system for heterogeneous catalysis.

PS–HDODA copolymer beads can be synthesized by suspension polymerization and functionalized by sulphonation using con. Sulfuric acid, and the ion exchange capacity of the obtained resins were determined by salt splitting titration. Metal ions can be loaded into the polymeric support by equilibrating the polymeric ligand with the metal salt solution. The metal loaded to the polymeric support was reduced into the nano scale by sodium borohydride. Sulphonated resin showed swelling in polar solvents indicating the presence of hydrophilic group in the polymeric system. Before sulphonation PS-HDODA copolymer beads showed no ion-exchange capacity due to the absence of sulphonic acid group.

The catalytic activity of prepared silver nanoparticles stabilized in polymeric hydrogel can be tested against p-NP reduction reaction. The catalyst showed 93% efficiency in the reduction reaction within 24 min from the start of the reaction. Sulphonated PS-HDODA system can be successfully utilized as supporting material for preparation and storage of stable silver nanoparticles and the supported catalyst system can be efficiently used for the treatment of wastewater containing p-NP.

Conflict of interest

The author declare that there is no conflict of interest regarding the publication of this chapter.

Author details

Jaya T. Varkey
Department of Chemistry, St. Teresa's College (Autonomous),
Ernakulam, Kochi, Kerala, India

*Address all correspondence to: jayavarkey@yahoo.com

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